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SPECTRAL PROPERTIES OF PASSIVELY Q-SPOILED LASERS

SemiAnnual Technical Summary Report

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ABSTRACT

Experiments demonstrating stimulated emission of organic dyes in the visible region by pumping with laser second harmonic frequencies are described. The demonstration of efficient spectral narrowing and tunability over a wide spectral range in both liquid and solid organic dye lasers is described. A discussion is given of experiments concerned with the photo and thermal response of polymethine dyes used for Q-spoiling the Nd laser. Two articles, one published and one in press, both supported by this contract, are reproduced as appendices.

FOREWORD

This report was prepared jointly by the Optical Physics and the Chemical Physics Divisions of Korad Corporation, Santa Monica, California, under Contract Nonr-5100 (00) entitled "Spectral Properties of Passively Q-Spoiled Lasers". The study was conducted under the project leadership of B. H. Soffer, with R. C. Pastor, H. Kimura, and B. B. McFarland participating.

Section 1

INTRODUCTION

The objective of this program is an experimental research study of the spectral properties of passively Q-spoiled lasers. The study is directed toward gaining further insight into the mechanisms of spectral relaxation and diffusion in laser materials and the physical behavior of passive Q-spoiling materials.

The distinction between these two classes of materials has been diminished because of the recent demonstration of stimulated emission from organic dye Q-spoiling materials as well as from other organic dye solutions. During this report period we have turned our attention to the interesting problems associated with these lasers. We report here on studies of visible stimulated emission in organic dyes induced by laser second harmonic pumping and studies of continuously-tunable narrow-band solid and liquid organic dye lasers. Additional results on photo and thermochemical processes in the 1.06-micron Q-spoiling organic dye solutions are also reported.

Section 2

TECHNICAL DISCUSSION

A. Stimulated Emission in Organic Dyes

(1) Visible Stimulated Emission from Organic Dyes

Organic dyes have recently been shown to exhibit stimulated emission when excited with the high brightness of a ruby laser. These dyes have consequently emitted radiation in the near infrared. We have demonstrated efficient laser emission in the visible region using dyes such as the rhodamines and fluorescein. Dyes in the xanthene and related families have conspicuously high fluorescent quantum efficiencies -- the more commonly available ones having their absorption bands located in the ultraviolet and blue-green, precluding direct pumping with such lasers as the ruby or neodymium high-power laser. Pumping was accomplished, transverse to the laser cavity, with the second harmonic of ruby or neodymium lasers at power levels of $\sim 10 \text{ Mw/cm}^2$ (see Figure 1 of Appendix A). Conversion efficiencies of more than 15% were obtained. The output beam angle of the dye laser can be narrower than that of the laser pump when the pumping is uniform as in the case of axial pumping. Over-all brightness gains have thus been realized. Thresholds, depolarization effects upon the pumping radiation, and other particular details are given in Appendix A, a reprint of a recent publication describing this work. It is noteworthy that the organic dye solution laser emits a spectrally variable and spectrally broad pulse up to some hundreds of wavenumbers wide, depending upon dye concentration, cavity length, and conditions of cavity gain (see Figure 2 of Appendix A).

(2) Continuously-Tunable Narrow-Band Organic Dye Lasers

We have demonstrated efficient spectral narrowing and continuous tunability in organic dye lasers over bandwidths that

are large compared to the ordinary lasing action by using diffraction gratings as cavity reflectors (see Figure 1 on Page 4). These effects have been demonstrated in the visible spectrum with rhodamine 6G and in the near infrared with a carbocyanine dye. With a particular rhodamine laser, for example, the spectral bandwidth was reduced from 60 \AA to a single line of width 0.6 \AA when a grating of 2160 \AA/mm was employed. The efficiency of this spectral "condensation" was approximately 70% in the region of normal dye lasing action where peak output is obtained. The range of tunability at the half-power points was some 200 \AA , a value greater than the bandwidth of normal lasing action (see Figure 1, Appendix B). Powers were in the range of 2×10^6 watts, but no attempt has yet been made to optimize or maximize this value.

Similar results were obtained with a solid sample of rhodamine 6G in polymethylmethacrylate pumped with the second harmonic of a Nd laser, the first demonstration of organic singlet-singlet lasing in the solid state. Furthermore, similar tunable lasing behavior was obtained in the near infrared region with 3,3' diethyl-thia-tricarbocyanine iodide in ethanol, pumping with a ruby laser. Additional details of the continuously tunable lasers are given in Appendix B, a preprint of a forthcoming publication describing this work.

(3) Conclusions

The spectrally broad output of the various families of dyes thus far successfully employed as organic dye lasers has led observers to consider them as primarily inhomogeneously broadened systems. Broadening of the spectral emission with higher cavity gain conditions further supports this outlook. The high relative efficiency of narrow line emission we observe, however, points out the need for qualifying this view.

It is expected that many related dye families will behave in a similar fashion and that the entire wavelength domain,

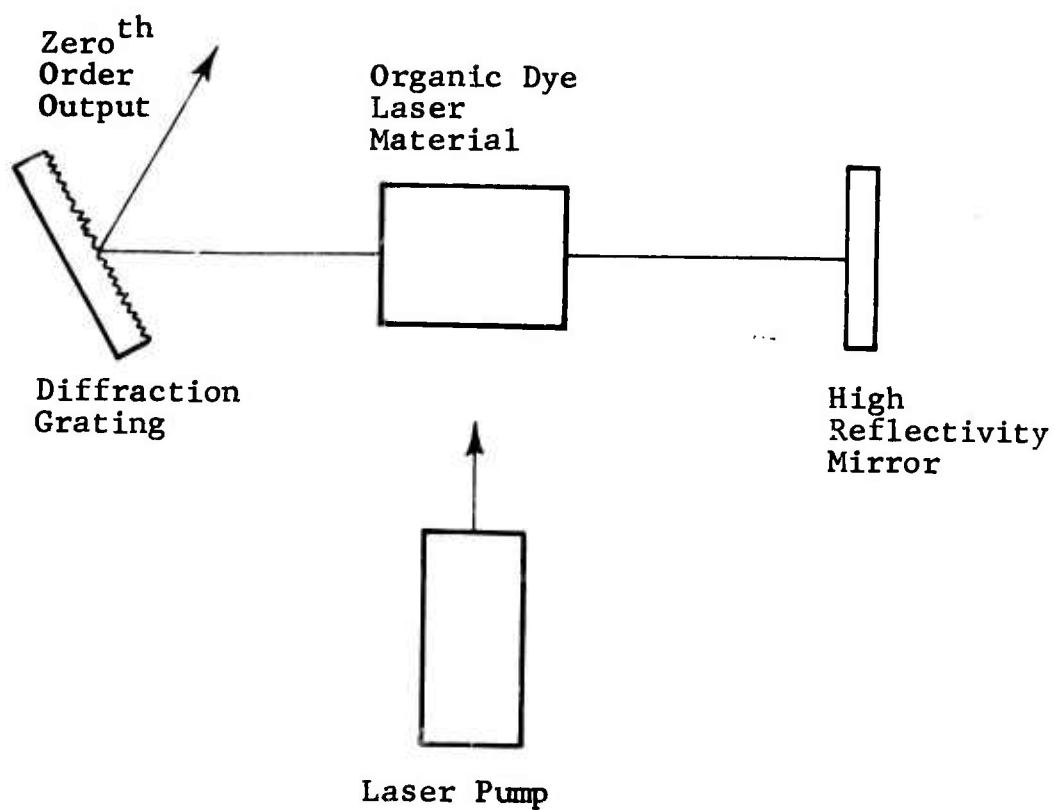


Figure 1
Schematic Diagram of Tunable Dye Laser

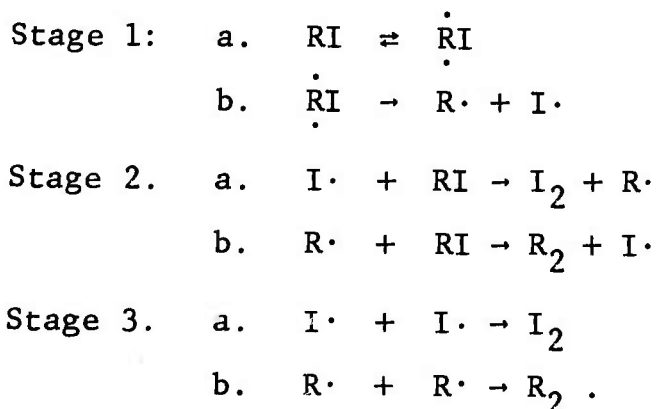
from 347 mμ (ruby second harmonic) to about 1 μ, could be practicably spanned according to these techniques.

Reversible and Irreversible
B. Bleaching of Dyes for Passive Q-Spoiling

In the previous SemiAnnual Technical Summary Report, dated November 1966, a model was presented which provided the working basis for a study of the reversible and irreversible bleaching of Q-spoiling dye solutions. The environmental stabilities of interest were of three kinds -- thermal, photo, and chemical.

The first feature bears on the problem of local heating during repetitive pulsing. The second feature is of interest from the standpoint of storage (ambient light) and radiation leakage from the flashlamp. The third feature is only pertinent to realistic contaminants when the solution is left open to air (e.g., H₂O, CO₂, and O₂).

At the working concentrations employed ($\sim 10^{15} \text{ cm}^{-3}$), the mole ratio of solvent to dye is 10^7 . The three-stage scheme for the homogeneous-phase decay of a very dilute solution of a dye iodide (RI) is as follows.¹ (RI is the triplet state.)



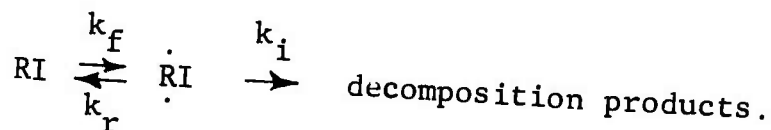
With the exception of Stage 1.a. (reversible bleaching), only the forward direction is considered for the case of a very dilute solution, to which the present investigation is limited. Stage 1 is akin to an induction period and assumes an electronic isomer as

¹ The symbol RI also stands for the molecule in the ground state (singlet).

an intermediate to dissociation, i.e., free-radical generation. Stage 2 is chain propagation, a cyclic reaction in competition with Stage 1.a. for RI (irreversible bleaching). Stage 3 is chain termination, which acts as a governor to the runaway character of Stage 2.

(1) Thermal Bleaching

In the scheme given, the limiting rate stems from Stage 1. This gives the following model for reversible and irreversible thermal bleaching.



Model
(1)

The k coefficients stand for specific reaction rates.

Such a model explained the kinetics of thermal bleaching in the temperature range $25^\circ - 180^\circ \text{ C}$. The enthalpy change, derived from the temperature dependence of the equilibrium constant, $K = k_f/k_r$, was seen to be equal to the activation energy derived from the temperature dependence of k_f . This meant that k_r was temperature independent in the range investigated. The triplet was calculated to be 7 kcal mole^{-1} above the ground state. The half-life for the radiationless transition of the triplet to the ground state, $\tau_r = 0.693/k_r$, was found to be $\sim 3.5 \text{ min}$.

In terms of optical spectra (see, for example, Figure 2 on Page 8), thermal bleaching is seen as a general reduction in the absorption with no isobestic point. We can, therefore, treat the bleaching kinetics of the thermal behavior without the complication of geometric isomerism.

(2) Radiation Bleaching

Bleaching by irradiation at 0.365μ vs time was found to be a zero-order process, a strong indication in the dilute

case that Stage 1 remained the limiting rate. The results show the absence of catalytic (and autocatalytic) breakdown. The solutions were air-free and were sealed off in vacuum.

At the tail end of the bleaching process, the slope decreased in magnitude monotonically. This is interpreted to be due to the throttling of Stage 2 by Stage 3. It should be noted that, from Stage 1.b. and on, bleaching is irreversible.

Figure 2 shows the room temperature absorption spectra of KQS (Korad dye) after a constant-intensity irradiation at 0.365μ for zero, one, and four minutes. The decay of the 1μ band is accompanied by an increase in the absorption at 0.37μ larger than at 0.45μ and 0.52μ , with an isobestic point evident.² The inserted figure shows that the increase in absorption at 0.37μ above that which corresponds to reversible bleaching can be accounted for by iodine in quinoline (see Stage 3.a.).

From the total bleaching effected at room temperature, it is calculated that for every photon absorbed 3×10^{-4} molecules of RI, the ground singlet species, disappear. Yet, under these conditions, bleaching is predominantly reversible (recovery, $\geq 90\%$), in agreement with Stage 1.b. where the half-life at room temperature, from the thermal decay, is $\sim 10^{10}$ min.³ Reversible bleaching signifies that the photodissociation equivalent of Stage 1.a. plus Stage 1.b. may be neglected under these conditions. Any buildup in the radicals $R\cdot$ and $I\cdot$ would have brought about rapid irreversible bleaching by Stage 2.

² These three absorption bands belong to the original species. The relative intensity depends on the solvent.

³ Using the same photon flux intensity at 0.365μ , and irradiating at 40°C to effect a bleaching of $\sim 50\%$, the recovery is 100%, essentially.

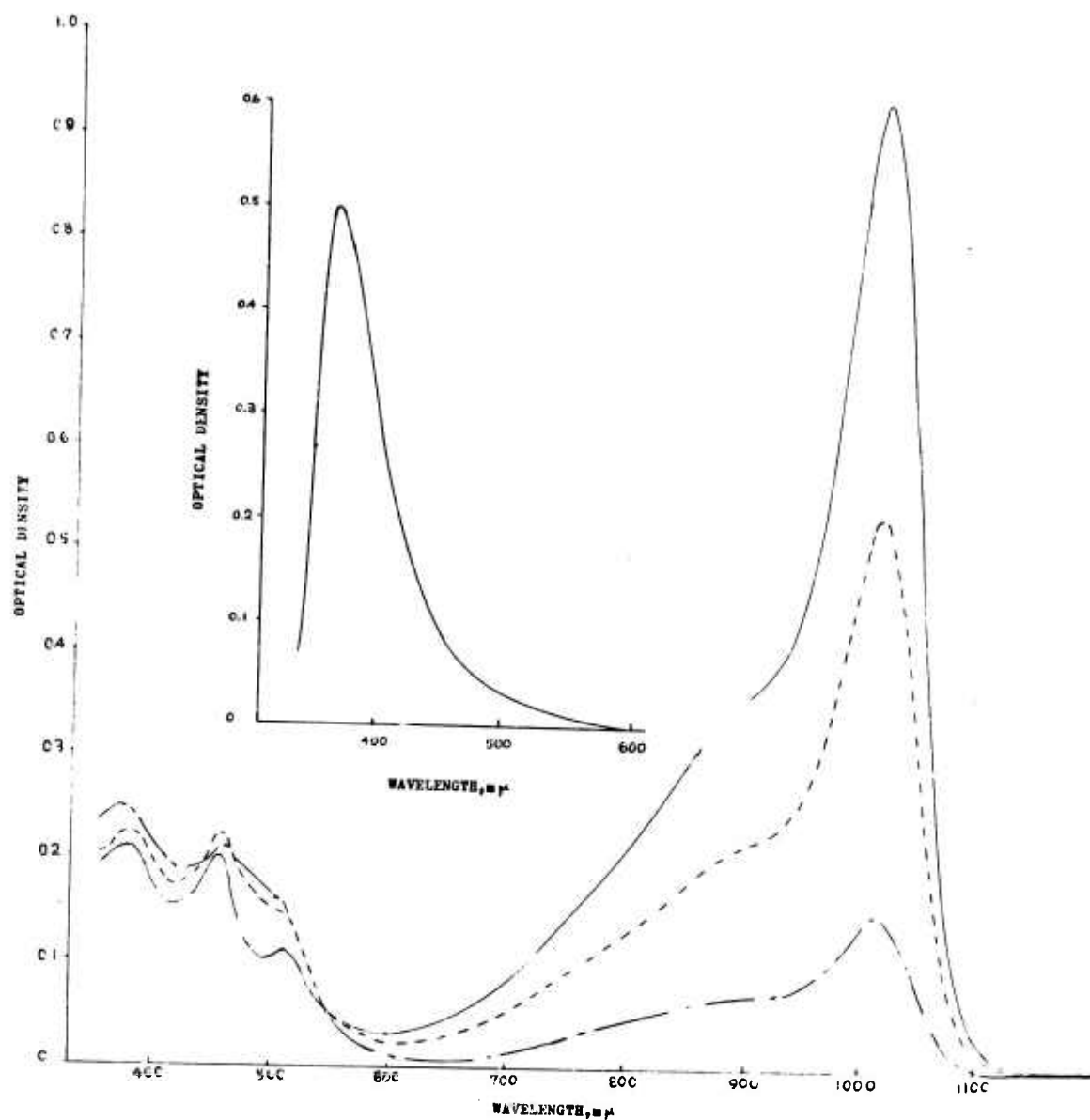


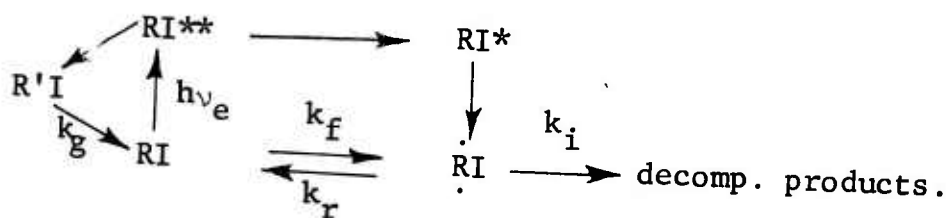
Figure 2

Quasi-Reversible Photochemical Process in Korad Dye (KQS)

- Room Temperature Absorption Spectrum of Korad Dye in Quinoline
- After 7 joules/cc of 365 $m\mu$ Radiation Absorbed
- .-.-.- After 32 joules/cc Absorbed
- Insert: Absorption Spectrum of the Iodine-Quinoline System

Reversible bleaching cannot be due solely to triplet-state trapping. The isobestic point in Figure 2 indicates another source -- excitation at 0.365μ leads to geometric isomerism.⁴ The absorption at 0.9μ is attributed to the cis arrangements while that at 1μ is attributed to the trans.⁵ Without going through the refinement of resolving the spectral envelope, the ratio of the absorption at 0.9μ to 1μ is readily seen in Figure 2 to be 0.36, 0.39, and 0.50 for zero, one, and four minutes respectively. This suggests an increase in the contribution of the cis forms.

Further additions to Model (1) must be considered to account for the response to the more energetic radiation, $h\nu_e$.



Model
(2)

The superscript (**) refers to an electronic excitation higher than (*), the first excited singlet, and R'I is the ground state (singlet) of a geometric isomer of RI.

It is assumed that the branching at RI** favors electronic over geometric isomerism. In the case of electronic isomerism, the cycle $\text{RI} \rightarrow \text{RI}^{**} \rightarrow \text{RI}^* \rightarrow \text{RI}$ is very rapid. Therefore, after irradiation, bleaching recovery comes only from the k_r path. In the case of geometric isomerism, the following path is not

⁴ It was established earlier that geometric isomerism is not sensibly effected through the fundamental electronic absorption, i.e., 1μ band. (See previous SemiAnnual Technical Summary Report, of November 1966.)

⁵ L.G.S. Brooker, p. 573, "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields", edited by T.S. Gore, B.S. Joshi, S.V. Sunthakar, and B.D. Tilak (Academic Press, 1962).

limiting: $RI^{**} \rightarrow R'I^* \rightarrow R'I$. Consequently, the limiting rate comes only from the k_g path. Hence, after irradiation, the two parallel paths for the regeneration of RI are k_r and k_g .⁶

In agreement with Model (2), the recovery from bleaching vs time after irradiation can be described as a linear superposition of two first-order processes. Five such curves, in the temperature range from 12° C to 45° C, were analyzed. Curve fitting by a method of least squares gave, for the k_r path, a half-life of $\tau_r = 3.3 \pm 0.6$ min, in good agreement with the rate obtained from the thermal response in B.1. From the Arrhenius expression for the rate, an energy barrier ≈ 1.6 kcal mole⁻¹ results from the temperature variation of k_r , limited by its root-mean-square deviation from the mean. The activation can hardly be called an energy barrier, since the value is easily accommodated intramolecularly by a vibrational transition. The latter feature is also in agreement with the result derived from thermal studies in B.1.

The rate analysis pertaining to geometric isomerism yields $\tau_g \approx 130 \pm 40$ min. From the root-mean-square deviation ($\pm 30\%$), it follows that the energy barrier is $\lesssim 2.8$ kcal mole⁻¹. Again, for the same reasons given in the preceding paragraph, the activation can hardly be called an energy barrier.

From these measurements it is deduced that the branching ratio at RI^{**} , electronic vs geometric isomerism, is better than 10:1, in agreement with the assumption made earlier. A direct test of the model would be to carry out a more exhaustive bleaching (irradiation time $\gg \tau_r$) under essentially reversible conditions and probe the optical absorption of $R'I$.

⁶ The population of $\dot{R}'I$ can be neglected because of two unfavorable branching ratios in series, the first at RI^{**} and the second at $R'I^*$.

(3) Chemical Bleaching

Reversible bleaching of these solutions can be demonstrated through control of pH, a behavior seen in indicators. However, this feature is not of interest in the present study.

Since radicals are generated (see Stage 1), the solution is expected to be reactive to other chemical species. The subsequent bleaching is irreversible. These responses are complicated either by dependence on thermal state or exposure to radiation. In certain cases it is possible to assess stability with respect to a given species at constant temperature, in the dark.

The choice of solvent has been employed to shift the fundamental absorption to effect a better matching for Q-spoiling. It is known that a fine change in the structure of the spectra, through a change in the distribution of cis and trans arrangements, accompanies solvation.⁵ In addition, chemical reactivity is influenced. Thus, irreversible bleaching by oxygen of the air, in the dark, at room temperature, using spectroscopic-grade solvents for KQS, gave a half-life of 120 hr for chlorobenzene, 6 hr for quinoline (3 hr if the solvent has had previous exposure), and 3.7 hr for methanol.

If the solutions are exposed to room light (fluorescent lamps), the decomposition is faster in each case and appears fastest with chlorobenzene. In the latter case, the speed is diffusion-limited suggesting a free-radical type reaction. However, the similarity in the spectra of the decomposed chlorobenzene solution in air with that which was air-free, sealed off in vacuum, and decomposed by Q-spoiling, led one to suspect that the oxygen may be serving as a catalyst, participating in some loose combination.

The effect of light, increasing the bleaching speed by many orders of magnitude, is probably due to Stage 1.a. (i.e., the triplet state). Air-free quinoline solution of KQS, sealed off in vacuum, shows fair stability to room light. Bleaching

by oxygen is sensitive to the presence of moisture which feature, unfortunately, was not controlled in the comparison of spectroscopic-grade solvents (see the preceding discussion and note especially the case of quinoline). Thus, in the case of two samples of KQS in vacuum-distilled quinoline, sealed off with 0.42 mm and 1.00 mm oxygen, the half-life in the dark, followed over a 300 hr interval, was 163 ± 6 hr at room temperature. From the specific reaction rate obtained by thermal bleaching, the only species which can be produced at a non-limiting rate is the triplet state.⁷

As pointed out in the scheme, Stage 3 is a throttle to Stage 2. If iodine is added to the dye solution, a net reverse direction of Stage 3.a. exists momentarily and manifests a rapid consumption of RI by means of Stage 2. The dissociation constant of I_2 in solution is 10^{-22} mole liter⁻¹.⁸ A 10^{-5} molar solution of KQS in methanol, mixed with iodine to form a 10^{-4} molar solution in I_2 , decays completely -- faster than the mixing rate. The concentration of iodine atoms is of the order of 10^{-13} molar. Thus, for each iodine atom, $\sim 10^8$ RI species cm⁻³ are eliminated in Stage 2. Irreversible (chemical) bleaching does not occur when a reducing agent is present in KQS in quinoline or chlorobenzene, and kryptocyanine in methanol.

(4) Stabilization of KQS in Chlorobenzene for Q-Spoiling

The runaway nature of chain propagation, Stage 1.b. to Stage 2, by adding iodine solution, was shown in B.3. to be blocked by the reducing agent. Thus, the latter reagent is an effective inhibitor from Stage 1.b. to Stage 2.a. However, to render a fair gauge of the stabilization effect of the agent,

⁷ The reaction between oxygen and $\dot{R}I$ would appear to be faster than k_f and k_i . A neat application of thermal bleaching with oxygen (in the dark) is the measurement of k_f and the triplet energy separation from the ground state.

⁸ C. Walling, "Free Radicals in Solution", p. 377 (Wiley, 1957).

the solution was shielded from flashlamp UV radiation. Unless this precaution is observed, it is seen in Model (2) that an efficient bleaching, reversible and irreversible, results. In agreement with the model, it was indeed verified that photobleaching by UV, reversible and irreversible, remained uninfluenced by the presence of the reducing agent.

Two cells of $\sim 3 \text{ cm}^3$ volume were employed to Q-spoil a 10 pps repetition rate Nd-YAG laser. Both had a few drops of methanol added, but in one the alcohol was saturated with the reducing agent. The optical densities at the wavelength of peak absorption were 1.0 with the agent and 0.9 without.

The input to the cell containing the reducing agent was 26 j. The output was 33.8 mj till 4.5×10^3 shots, when the laser failed temporarily; 25.0 mj till 7.5×10^4 shots; 20.5 mj thereafter till 1.19×10^5 shots; 19.0 mj at 1.30×10^5 shots; and 19.0 mj at 1.55×10^5 shots. Double-pulsing occurred after 1.55×10^5 shots when the optical density was reduced to 0.60. The powers were $\sim 3 \text{ mW}$ peak for the majority of shots. Breakdown occurred at the glass-solution interface. A black smudge, approximately circular and $\sim 1 \text{ mm}$ in diameter, formed slightly below the center of the beam traversal. The failure could have been due to an inhomogeneous power density across the beam. Sixty-eight hours later, the O.D. climbed up to 0.63, a recovery from reversible (thermal) bleaching due to the slight heating concomitant with Q-spoiling.

Without the reducing agent, the input was a bit lower, 23.7 j. The output started at 29.4 mj, slowly fell to 22 mj at 2.39×10^4 shots when the pulses began to double. Six hours later the O.D. had dropped to 0.21 and 60 hrs later it was 0.10, an indication that Stages 2 and 3 were well underway. The color was red in this cell.

(5) Bleaching by Heterogeneous Paths

The reversible aspect of bleaching is based on adsorption. Sorption equilibrium provides a technique for buffering small

changes in dye concentration. As a rule, the sorbed state of the dye shows greater instability. Consequently, the feature of reversible bleaching in a heterogeneous process is of no interest.

The instability of the sorbed state is easily demonstrated with kryptocyanine. The dye solution in methanol is quite stable in the open and is employed for Q-spoiling at 0.69 μ . If a filter paper strip is dipped in the solution and allowed to dry, the blue color is seen to fade within a day. It is easily shown that oxygen and light are necessary, but neither one is sufficient. Similar instabilities are seen on inorganic oxide substrates, e.g., silica, alumina, etc.

Very rapid decomposition, presumably diffusion-limited, of KQS in various solvents occurs following the introduction of copper. Undoubtedly, the phenomenon can be shown for other dyes and metals.

As would be expected, increasing the interface area between gas (oxygen) and liquid (KQS solution in quinoline) hastens decomposition. The following sequence, carried out at room temperature (in the dark), typifies the response encountered: Dry O_2 bubbled through yielded a half-life of $\tau = 4$ hr; followed by dry N_2 , after allowing for the flushing of the oxygen, showed no decomposition in 15 hr; then wet N_2 gave a slow decomposition, $\tau = 30$ hr; and finally with wet O_2 a rapid decomposition, $\tau = 0.13$ hr. (See B.3.). It is also of interest to mention that bubbling O_2 through a 10^{-5} molar solution KQS in methanol gives a first-order decomposition, $\tau = 0.4$ hr. However, with a reducing agent, the decay was zero-order, requiring 1 hr for complete decomposition.

Finally, it should be pointed out that interface carbonization (or tar?) breakdown during Q-spoiling occurs with KQS in either quinoline or chlorobenzene. In addition, we have realized cases where a considerable black deposit is formed with no significant reduction in the optical density (absorption

of the dye). This is clearly a case of breakdown of the solvent at the interface, most likely a chain reaction triggered by a small concentration of radicals generated from the dye.

(6) Conclusions

Under environmental conditions pertinent to Q-spoiling, electronic isomerism via the triplet state, an intermediate in the homogeneous-phase breakdown of the dye, correlates the results observed in reversible and irreversible bleaching. Q-spoiled bleaching leads to trapping in the triplet by two paths. Both involve intersystem crossing, either from the first excited or the ground singlet. The latter is characterized by k_f and its relaxation back to the ground state by k_r . Although k_f is dependent on intermolecular collisions, it appears that k_r is essentially intramolecular and remains unperturbed over a wide temperature range.

Three favorable kinetic relations for Q-spoiling solutions are:-

- (a) inefficient branching at RI^* ,
- (b) $k_f \ll k_r$, and
- (c) k_r commensurate with (a) and pulse rep rate.

All three, as well as the temperature dependence of k_f , are dependent on an inner and outer bound on E_t , the energy separation of the triplet state:

$$E_s \gg E_t < RT_{ss} ,$$

where E_s is the separation of the first excited singlet and T_{ss} is the steady-state temperature corresponding to the pulse rep rate. From the model it appears that the long wavelength limit for Q-spoiling solutions operating at room temperature is not far above 1μ . The model explains Brooker's findings.⁵ As longer chain-lengths are employed to push the fundamental absorption past 1μ , the extinction coefficient falls rapidly, the absorption becomes flat, and the dye is more unstable.

In reversible bleaching arising from Q-spoiling, one can neglect the effect of geometric isomerism which has an insignificant branching ratio from the first excited singlet. However, this is not the case for the more energetic photons and the results show the merit of shielding the solution from flashlamp UV radiation. With UV radiation, reversible bleaching through geometric isomerism is possible and limits the effectiveness of the solution for Q-spoiling. The room-temperature lifetime for the regeneration of RI, the ground singlet species, is forty times larger than the regeneration lifetime from the triplet state. The frequency factor for the transition rate (geometric isomerism) appears low in view of the fact that no large energy barrier is seen in the results. It is to be expected that geometric isomerism, compared to electronic isomerism, is the more sluggish.

The scheme for the homogeneous reaction path has proven to be a heuristic working model. The homogeneous phase has achieved a stability where the limitation is set by a breakdown via a heterogeneous path. The latter circumstance presents an entirely different problem and deserves a separate study.

Section 3
PLANS FOR NEXT PERIOD

A concluding phase of the study reported on the decay kinetics of Q-spoiling dyes is in progress. These results will be incorporated into a paper which will be submitted for approval shortly. Further work on the continuously-tunable organic dye laser will be performed with special attention directed to the relationship between pumping uniformity, beam angle, and spectral width.

APPENDIX A

Laser Second-Harmonic-Induced
Stimulated Emission of Organic Dyes

LASER SECOND-HARMONIC-INDUCED STIMULATED EMISSION OF ORGANIC DYES*

B. B. McFarland

Korad Corporation

A Subsidiary of Union Carbide Corporation

Santa Monica, California

(Received 27 February 1967)

Solutions of several dyes of the fluorescein family have been made to exhibit stimulated emission in the visible when excited by ruby and neodymium second harmonics. Oscillation threshold and conversion efficiencies are given. Depolarization effects in the emission are described.

Recent investigations have pointed out the feasibility¹⁻³ and the practicality⁴ of stimulated emission from laser-excited solutions of organic dyes (hereafter designated laser-pumped laser or LPL). All of the dyes reported to date have been excited with ruby lasers and emitted in the near infrared. This Letter describes the first observation of efficient LPL emission in the visible region of the spectrum obtained by laser second-harmonic excitation.

It is well known that dyes of the fluorescein family have nearly-unity fluorescent efficiencies, thus making them likely candidates for dye solution lasers. Their absorption bands are located in the ultra-violet and blue-green, precluding direct pumping with currently available high-power lasers such as ruby or neodymium. The author has found that effective pumping can be accomplished with the second harmonic of ruby or neodymium lasers

generated in phase-matched ADP crystals. The experimental arrangement employed is shown schematically in Fig. 1. (Mirrors R_1 and R_2 had reflectivities nominally 99% and 50% respectively.) Using a Korad K1QP ruby or neodymium glass laser as the fundamental source, approximately 10 MW/cm^2 of unfocused $347\text{-m}\mu$ or $530\text{-m}\mu$ radiation was available at the dye cell.

Several dyes of the fluorescein family were in-

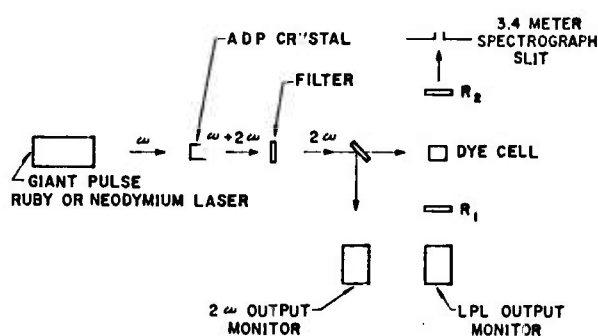


Fig. 1. Schematic diagram of experimental apparatus. $\vec{E}_{2\omega}$ is normal to the page.

*This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense [Nour 4130-(00)].

investigated using one or both of the generated harmonics. Examples of the dyes exhibiting stimulated emission are listed in Table I. The wavelength of peak emission was determined with a 3.4-m Jarrell-Ash spectrograph. The right-hand column of the table indicates the wavelength of the exciting source. The values of λ given in the table are representative owing to the shift to longer λ characteristically accompanying an increase in dye concentration.^{2,3} Figure 2, which is a plot of emission wavelength vs absorption coefficient for rhodamine-6G in ethyl alcohol, is typical of all the dyes listed in Table I. This wavelength shift is a consequence of the effects of self-absorption.² The spectral bandwidth of the laser emission of all the dyes listed in Table I were very broad; typically 50 to 100 Å.

Rhodamine-6G was selected for more detailed investigation since the location of its absorption band permits effective excitation with either ruby or neodymium laser second harmonic. More than 15% conversion of second-harmonic light to LPL emission, using either of the harmonics, was obtained from a 1.7-cm path length cell containing 2×10^{15} molecules/cm³ of rhodamine-6G dissolved in ethyl alcohol. The absolute output, measured calorimetrically, was 0.012 J with a 5-nanosecond pulse width. Oscillation threshold in this configuration was achieved with 1.4 MW/cm² of 347-m μ radiation. This solution was then diluted to give the same absorption coefficient at 530 m μ (the absorption cross section (σ) at 347 m μ is 1/10 the σ at 530 m μ) and threshold was determined using neodymium second harmonic. The results indicate that

Dye	Solvent	Laser Wave-length (m μ)	Source Wave-length (m μ)
Fluorescein (disodium salt)	water	535	347
Acriflavin hydrochloride	ethyl alcohol	510	347
Rhodamine-B	"	577	347, 530
Rhodamine-G	"	585	347, 530
Rhodamine-6G	"	565	347, 530

the same power density (within 50%) is required of both sources to achieve oscillation.

One of the interesting aspects of exciting the same dye with two different monochromatic sources concerns the polarization of the LPL emission. The depolarization of molecular fluorescence and its absorption wavelength dependence has been studied extensively.⁵ Many dyes, notably the rhodamines, exhibit a negative polarization when excited by uv and a positive polarization when excited by visible radiation.

When rhodamine-6G in ethyl alcohol was excited with ruby second harmonic at a power level approximately 4 times oscillation threshold, the LPL emission was predominantly polarized normal to the pump electric field. The measured polarization was $P = -0.9$. When this same dye was excited by 530-m μ radiation, sufficient depolarization occurs to cause the LPL emission to be polarized parallel to the exciting field (i.e., $P = +1$). This phenomenon, which has not been previously reported in stimulated emission, may well provide a useful method for the study of intramolecular cross-relaxation processes.

The author thanks Dr. R. H. Hoskins and B. H. Soffer for helpful suggestions and discussions.

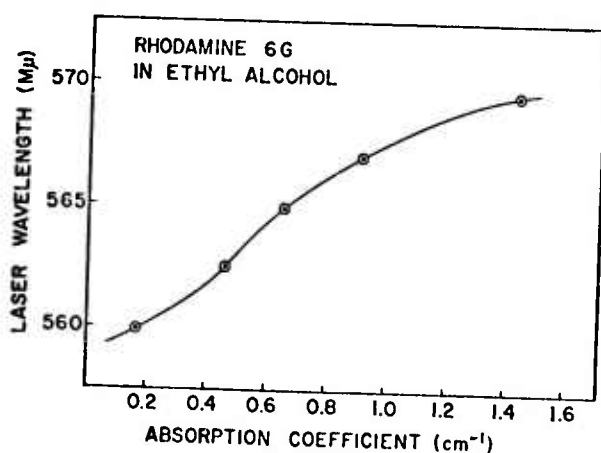


Fig. 2. LPL emission wavelength vs absorption coefficient for rhodamine-6G dissolved in ethyl alcohol.

¹P. P. Sorokin and J. R. Lankard, *IBM J. of Res. and Dev.* **10**, 162 (1966).

²M. L. Spaeth and D. P. Bortfeld, *Appl Phys Letters* **9**, 179 (1966).

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⁴P. P. Sorokin, W. H. Culver, E. C. Hammond, and J. R. Lankard, *IBM J. of Res. and Dev.* **10**, 101 (1966).

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APPENDIX B

Continuously Tunable Narrow Band Organic Dye Lasers

CONTINUOUSLY TUNABLE NARROW BAND ORGANIC DYE LASERS*

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A B S T R A C T

Efficient spectral narrowing, and tunability over a wide spectral range, has been demonstrated in solid and liquid organic dye lasers using diffraction gratings as cavity reflectors.

*This research is part of Project DEFENDER under the Joint Sponsorship of the Advanced Research Projects Agency, the Office of Naval Research, and the Department of Defense.

The organic dye solution laser (1) has been observed to emit a spectrally broad pulse up to some hundreds of wave numbers wide, depending upon dye concentration, cavity length, and conditions of cavity gain. We report in this letter efficient spectral narrowing and continuous tunability in dye lasers over bandwidths large compared to the ordinary lasing action, by use of diffraction gratings as cavity reflectors. We have demonstrated this effect with members of the xanthene and carbocyanine dye families. We further report the use of solid solutions of dyes in plastic as a practical dye laser material.

A typical experiment using alcoholic solutions of Rhodamine 6G as the laser material will be described in detail. Ethanol solutions with decadic absorption coefficients 0.74 cm^{-1} and 0.20 cm^{-1} at $347 \text{ m}\mu$ were employed in a cubical glass cell, 1.75 cm internal dimension, with four sides polished. Optical densities are preferred to concentration values as the associated molecules of Rhodamine 6G in ethanol (2) have smaller

optical cross sections. This furthermore makes it impractical to precisely prepare solutions of desired density by dilution from a standard solution of known concentration. Pumping was effected transverse to the cavity axis using the 10^{-8} sec, 10^7 watt/cm² second harmonic output of a giant pulse ruby laser. The 12 cm long cavity consisted of a flat dielectric mirror of 95% reflectivity and a flat reflective diffraction grating with 2160 lines/mm blazed at 5000 Å first order with an approximately constant first order reflectivity of $80 \pm 3\%$ for the wavelengths of interest, i.e., longer than 5520 Å. The approximate constant reflectivity is a consequence of there being no second order for these wavelengths. The grating was used in the Littrow arrangement and the output from the laser was obtained via the zeroth order reflection or the small transmission of the dielectric reflector. Excepting the absolute power, all the measured characteristics of this laser were independent of this choice of outputs. Spectra were photographed with a 3.4m spectrograph and the energetic and temporal behavior of the laser were recorded with photo-

diodes calibrated calorimetrically. Beam angle was measured by a self-calibrating photographic technique (3).

The output of the laser was repeatedly measured using a set of dielectric mirrors of reflectivity approximating that of the grating. An output value for the reflectivity equaling that of the grating was found by interpolation. This value is normalized to one arbitrary unit when the high concentration of dye was employed (see Fig. 1). The absolute conversion efficiency was not optimized but was about 15%, yielding pulses in the 2×10^6 watt range, coupling via the zeroth order reflection. Replacing the grating, we obtained the set of data shown in the upper trace of Fig. 1 showing relative efficiency vs. wavelength of emission. The input pumping intensity was held approximately constant and the grating angle was varied to effect the tuning. Slight variations in input were normalized in the efficiency plot. Errors introduced here especially by the effects of multimoding upon the second harmonic generation, contribute

to the scatter of the data. Spectrograms taken simultaneously with this data, reveal the line-width of the emission to have narrowed from 60 Å using the all dielectric reflector cavity, to 0.6 Å when the grating was employed. The spectral condensation is seen to take place with ~ 70% efficiency in the region of the center of normal laser emission. The total available bandwidth is seen to be much greater than the bandwidth of the normal laser emission. In the lower trace of Fig. 1 we show the analogous results for a lesser dye concentration. Again the spectral condensation is seen to be efficient in the region of normal laser emission but here the normal laser emission itself is not as efficient as the case of higher concentration. Again the available bandwidth is greater than that of the normal laser of the same concentration. The tunable half-power bandwidth is closely the same for both concentrations, but shifted to longer wavelengths in the higher concentration case.

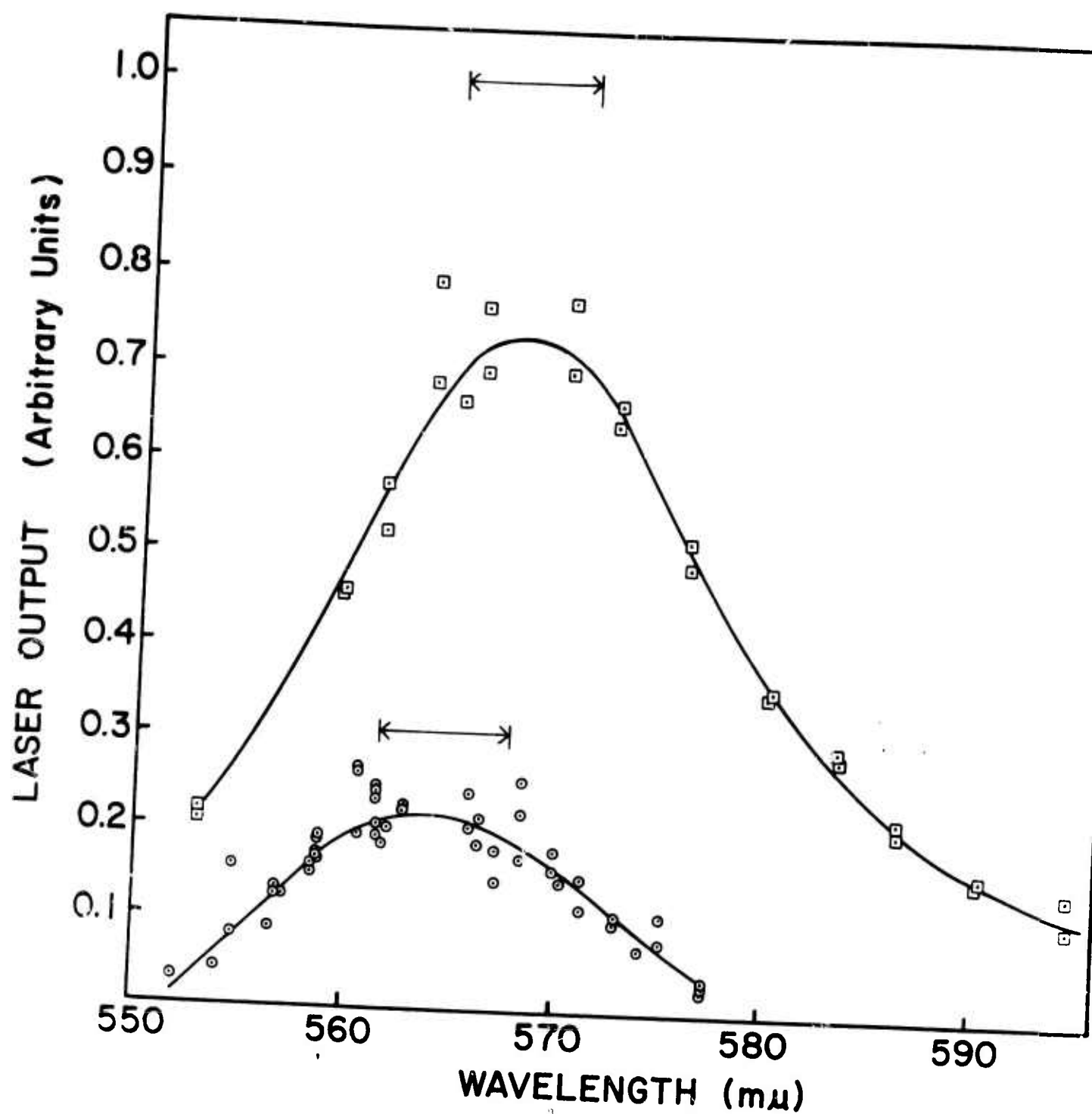
Beam angles in the plane of grating dispersion measuring $\sim 5 \times 10^{-3}$ rad, were too large

to account for the observed spectral narrowing by dispersion although we note that the temporal development of the integrated beam angle is presently unknown to us. The spectral content of the output was the same over the entire far field distribution. It should be noted that a grating with 4 times lesser dispersion produced spectral outputs 8 times as broad.

Similar results were obtained with a solid sample of Rhodamine 6G in polymethylmethacrylate, pumped with the second harmonic of a Nd laser. No room temperature phosphorescence could be detected in the Rhodamine solid solution. A strong phosphorescence, typical of some dyes in solid solution, would of course be detrimental to laser action. The use of the solid matrix obviates the problems of convective schlieren, evaporation, and cells. Furthermore, similar results were obtained with 3, 3' diethyl thiatricarbocyanine iodide in ethanol in the near infrared region pumping with Q-spoiled ruby laser. Alignment of the grating was effected using an image converter and autocollimator.

The broad spectral output of the various families of dyes thus far successfully employed as organic dye lasers (1) leads one to consider them as primarily inhomogeneously broadened systems. The high relative efficiency of narrow line emission reported in this work however, points out the need for qualifying this view.

It is expected that many related dye families will behave in a similar fashion and that the entire wavelength domain from 347 m μ (ruby second harmonic) to about 1 μ could be practicably spanned according to these techniques.



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
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
FIGURE CAPTION

Fig. 1 Relative efficiency of tunable
Rhodamine 6G laser vs. wavelength.

Upper trace:  Optical density 1.3
(347 mμ). Grating in
cavity.

 Dielectric reflectors.
Arrows indicate spectral
bandwidth for this case.

Lower trace:  Optical density 0.35
(347 mμ). Grating in
cavity.

 Dielectric reflectors.

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13. ABSTRACT Experiments demonstrating stimulated emission of organic dyes in the visible region by pumping with laser second harmonic frequencies are described. The demonstration of efficient spectral narrowing and tunability over a wide spectral range in both liquid and solid organic dye lasers is described. A discussion is also given of experiments concerned with the photo and thermal response of polymethine dyes used for Q-spoiling the Nd lasers. Two articles, one published and one in press, both supported by this contract, are reproduced as appendices.		

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